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(54) Title: MOLDABLE THERMOPLASTIC POLYMER FOAM BEADS

(57) Abstract

A continuous process for making moldable foam beads comprising a non-crosslinked or crosslinked thermoplastic polymer foam are produced by mixing a composition comprising a non-crosslinkable or crosslinkable thermoplastic polymer or a thermoplastic polymer with a crosslinking agent, additives to achieve specific properties, a blowing agent, extruding the admixture under pressure, crosslinking, when applicable, the admixture under pressure, modulating the admixtures temperature to achieve the desired foaming properties, and then expanding the admixture in a zone of lower pressure to form a foam bead that can be molded.

MOLDABLE THERMOPLASTIC POLYMER FOAM BEADS

FIELD OF THE INVENTION

The present invention concerns a process for making moldable beads of foamed thermoplastic polymers, and particularly beads of non-crosslinked and crosslinked thermoplastic polymers, such as polystyrene and non-crosslinked and crosslinked polyolefins, as well as any other foamable crosslinked and non-crosslinked thermoplastic polymers.

BACKGROUND OF THE INVENTION

Foamable polystyrene beads are relatively easy to make. In a typical method, polystyrene resin is impregnated with an expanding agent, usually pentane, during polymerization, or else resin particles are impregnated with the expanding agent after polymerization. These particles are then subjected to steam to partially expand them.

Foamable polystyrene beads are also easy to mold. In a typical method, the pre-expanded beads are fed into a mold and subjected to pressurized steam where they expand, fuse together, and conform to the shape of the mold. Such

foamed, silane-crosslinked polyolefin foam cable coverings which are described as relatively hard and rigid and are produced by extruding a mixture containing polyethylene, a silane hydrolyzable with water, a condensing catalyst and a foaming agent such as water.

U.S. Patent No. 4,333,898 discloses a method for the production of relatively high density foamed polymers (such as polyethylene) in which the polymer is mixed with a silane, which grafts thereto, and which is then extruded to provide a jacket for a cable or the like. A moist, inert gas is injected into the extruder just prior to extrusion to cause the polymer to foam and the silane-grafted polymer to crosslink.

U.S. Patent No. 4,456,704 discloses a method for producing crosslinked polyethylene foams. The method utilizes a mixture of a polyolefin resin, a blowing agent, and, optionally, a surface active agent. The polyolefin resin contains a crosslinkable ethylene polymer having on the side chains thereof silyl groups which effect crosslinking upon contact with water. The ingredients are mixed, and the mixture is extruded into a low pressure zone where the resulting extrudate (e.g., in sheet form) is allowed to expand. The expanded extrudate is then brought into contact with a silanol condensing catalyst so that the expanded extrudate is crosslinked upon contact with water.

U.S. Patent 4,606,873 discloses a process for making polystyrene beads, but does not mention polyolefins or crosslinking of the polyolefins prior to expansion.

U.S. Patent No. 4,870,111 discloses a process for making moldable foam beads comprising a silane-crosslinked polyolefin foam. The beads are made by mixing a composition comprising a silane-modified polyolefin (such as a silane-grafted polyethylene) and a silanol condensation catalyst in an extruder to produce a melt, then injecting a blowing agent into the melt at a rate effective to produce a desired foam density in the extrudate. The foamed polyolefin is then extruded and cut to form foam beads, and the beads are

exposed to moisture to produce silane crosslinking of the polyolefin foam.

The foregoing references do not disclose, recognize or appreciate the advantages of making a moldable, non-crosslinked or crosslinked thermoplastic polymer foam bead, such as those made from crosslinkable silane grafted polyolefins or chemically crosslinked polyolefins, according to the method and apparatus disclosed in the present application. The foregoing references also do not disclose, recognize or appreciate the advantages of such a method wherein the polyolefins are crosslinked before they are foamed to enhance the processing characteristics of the foam beads and to enhance the properties of the foam and articles made from the polyolefin foam beads. Such advantages include the increase of melt strength, smaller cell diameter, better cushioning characteristics, and higher melting points.

In addition, none of the aforementioned references disclose a method for the manufacture of a moldable non-crosslinked or crosslinked foam bead in which the bead comprises either (1) a non-crosslinked thermoplastic that is foamable; (2) a chemically crosslinked polyolefin, made from a mixture comprising a polyolefin with a chemical crosslinking agent that is placed in an extruder to produce a melt; or (3) a silane-crosslinked polyolefin foam made by mixing a composition comprising a silane-modified polyolefin (such as a silane-grafted polyethylene) and a silanol condensation catalyst in an extruder to produce a melt; injecting a blowing agent into the melt at a rate effective to produce a desired foam density in the extrudate; extruding the melt into a pressurized atmosphere that is sufficient to prevent appreciable expansion of the polyolefin; cutting the melt and thus forming non-foamed beads suspended in a conveying media, such as water; conveying the beads through a zone where they are crosslinked when required; conveying the beads through a zone where the temperature of the beads is regulated to a

desired or effective temperature for foaming; and expelling the beads to a lower pressure where they expand to form moldable non-crosslinked or crosslinked foam beads in a continuous manner.

Improved methods of producing moldable beads of foamed thermoplastic polymers, such as polyethylene or polypropylene, are clearly needed that do not require pressure treatment or radiation and that take advantage of the cellular orientation and strength achieved when expanding a polyolefin that is at its ideal extrusion temperature and/or that is already crosslinked.

SUMMARY OF THE INVENTION

The present invention provides a method of producing moldable expanded non-crosslinked or crosslinked thermoplastic polymer foam beads that requires only relatively simple, inexpensive equipment to implement. The method is such that the beads may be produced economically at any desired location, and in any desired quantity. Thermoplastic polymer foam beads and articles made according to the method of the present invention have a composite structure made up of an antistatic agent and/or a flame retardant agent which, when combined and produced in accordance with this invention, have improved usefulness because of their properties. The new thermoplastic polymer foam beads, including polyolefin foam beads, are produced in a single operation and cost substantially less to produce than those made with a coating process or by the secondary lamination of articles made from the beads.

Various types of antistatic additives and flame-retardant agents can be used to produce the thermoplastic polymer and polyolefin foam beads of the present invention. Furthermore, the foam beads can be made into a multitude of shapes, such as sheets, rods, planks or other forms. These products may be modified further by cutting, laminating or stacking.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic drawing of a conventional foam extruder and die;

FIG. 2 is a schematic drawing of a first embodiment of an extruder die suitable for use with the method of the present invention;

FIG. 3 is a schematic drawing of a second embodiment of an extruder die suitable for use with the method of the present invention;

FIG. 4 is a schematic drawing of the extruder assembly used to implement the methods of the present invention; and

FIG. 5 is a schematic drawing of a third embodiment of an extruder die suitable for use with the method of the present invention.

PREFERRED EMBODIMENTS OF THE INVENTION

These benefits and other advantages are achieved by combining antistatic and flame-retardant agents into a thermoplastic foam shape in a continuous process. The foam passes through a heated pliable state to a cooled set state during preparation, using a process described below.

Any thermoplastic polymer can be used in this invention to make moldable foam beads. One group of thermoplastics that has achieved market acceptance as a moldable foam bead is the polyolefins. Although any extrudable, foamable polyolefin composition maybe used, a polyolefin polymer that is solid under standard conditions is preferred. Exemplary preferred polyolefins include the organic addition polymers or copolymers of the monomers discussed below. Other appropriate polyolefins will be apparent to one skilled in the art.

In accordance with the present invention, moldable non-crosslinked or crosslinked polyolefin foam beads are produced. The polyolefin is preferably selected from the group consisting of medium density polyethylene, low density polyethylene, linear low-density polyethylene, polypropylene, polybutylene, and copolymers of olefin

monomers having from 2 to about 8 carbon atoms, and most preferably is low density or linear low density polyethylene.

Suitable polymers of ethylene, propylene, butene-1, and isobutene can be used. Also suitable are copolymers of these monomers, ethylene/vinyl acetate copolymers, ethylene/acrylic copolymers and the like. Blends of the above-named polymers and copolymers are also included. Especially preferred thermoplastic polymers are polyethylenes, ethylene/vinyl acetate copolymers, ethylene/acrylic acid copolymers, ethylene/methyl acrylic copolymers and ionomer salts of such acid copolymers. Any thermoplastic polymer and/or blend of polymers that is substantially non-crosslinked or crosslinked and that is foamable can also be used for the process described herein.

In practice, cellular thermoplastic polymer bodies are prepared in accordance with the present invention by blending a nucleating agent with a thermoplastic such as polystyrene, a polyolefin, a crosslinkable polyolefin, or a polyolefin and a crosslinking agent. Where required, a chemical blowing agent, an antistatic agent and/or a flame retardant agent or other additives may be used to enhance specific properties. The blend is then processed under pressure and is heated in a pressure-resistant vessel at temperatures between about 150° C to 230° C. When required, a blowing agent is injected into the vessel to form an admixture with the blend at a temperature at least as high as the melting point of the polymer, until a uniform or substantially uniform flowable gel is obtained. Thereafter, the admixture is extruded and discharged through a suitable orifice into a pressurized zone. The extruded material is cut into beads and is crosslinked when applicable, its temperature is adjusted to a desired and/or suitable range for foaming, and it is then expelled to a lower pressure where it foams and is then cooled.

The present invention provides an improved and economical method for making foam beads from thermoplastic

polymers such as polystyrene or polyolefin polymers. The foam beads are normally molded into shapes that are useful for a variety of purposes, such as insulation, flotation and protective packaging. The products possess a highly uniform, fine-cell structure consisting mainly of thin-walled, closed cells. The products made from the foam beads are flexible and tough. Finely divided solid materials, such as calcium silicate, zinc stearate, magnesium stearate, and the like, can advantageously be incorporated into the polymer or gel prior to expanding the same. These finely divided materials aid in controlling the size of the cells and are employed in amounts of from 0.01 to 10 percent by weight of the polymer.

This invention relates to expandable thermoplastic polymers, such as styrene or olefin polymer compositions and processes, and more particularly to expandable modified thermoplastic polymer compositions having dimensional stability and utilizing a blowing agent selected from, but not limited to, volatile organic compounds.

It is well known to prepare thermoplastic polymer foams by heat plastifying a normally solid thermoplastic polymer resin, admixing such heat plastified resin with a blowing agent under heat and pressure to form a flowable gel and thereafter extruding the gel into a zone of lower pressure and temperature to activate the blowing agent and expand and cool the gel to form the desired solid thermoplastic foam product.

However, a problem frequently encountered with some thermoplastic foams, especially polyolefins such as polyethylene, is that of preventing an unacceptable degree of shrinkage of partially cured foam during the aging or curing period following production of the foam. During the aging or curing period the blowing agent employed gradually diffuses out of the cells in the foam product and air gradually diffuses into the cells in place thereof. Until quite recently, it was believed that only one volatile hydrocarbon blowing agent, namely 1,2-

dichlorotetrafluoroethane, was capable of providing sufficient dimensional stability during the curing period to permit the commercially viable manufacture of low density (e.g., 1 to 6 lbs/ft^3, or 16 to 96 kg/m^3) foams of ethylenic polymer resins. That is, only dichlorotetrafluoroethane was believed to diffuse out of the foam cells slowly enough to prevent cell wall collapse while air was slowly diffusing into the cells.

More recently, permeability modifiers or stability control agents have been developed for incorporation into polyolefins in an attempt to slow the diffusion of volatile hydrocarbon blowing agents out of polyolefin foam cells. The objective of these permeability modifiers is to render the foams more dimensionally stable to a wider variety of volatile hydrocarbon blowing agents. For purposes of this invention, the terms "permeability modifier" and "stability control agent" will be used interchangeably and will refer to compositions incorporated into the polyolefin to slow diffusion of volatile hydrocarbon blowing agents from the foam cell walls. For example, Watanabe et al, U.S. Pat. No. 4,214,054, teaches the production of polyolefin foams utilizing volatile hydrocarbon blowing agents. Permeability modifiers such as saturated higher fatty acid amides, saturated higher aliphatic amines, and esters of saturated higher fatty acids are incorporated into the polyolefin composition prior to expansion.

U.S. Pat. No. 4,331,779 also teaches ethylenic polymer foams having improved dimensional stability and teaches the use of a copolymer of ethylene and an unsaturated carboxylic acid as a stability control agent. U.S. Pat. No. 4,347,329 teaches the use of a fatty acid amide such as stearamide for use in polyolefin foams as a stability control agent. U.S. Pat. No. 4,394,510 further teaches the use of fatty acid amide stability modifier agents to produce polyolefin foams having improved elevated temperature dimensional stability. Patent No. 3,644,230 discloses a method for preventing post extrusion cell collapse in polyolefin foams by the

incorporation of a small amount of a partial ester of a long chain fatty acid and a polyol. Patent No. 3,755,208 discloses a method for preventing post extrusion cell collapse in vinyl copolymer foams by the incorporation of a small amount of a partial ester of a long chain fatty acid and a polyol.

The use of such permeability modifiers permits the use of a wider variety of volatile blowing agents. The more inexpensive volatile blowing agents, such as isobutane, can be utilized in conjunction with stability control agents to stop shrinkage. When isobutane has been used alone as the blowing agent in polyolefin foams without the stability control agent, the foams exhibit maximum shrinkages defined as 100(1-r) of between 10 and 20%, where r = the ratio of the volume of foam on the day it is at a minimum to the volume of the foam immediately after expansion. See, i.e., Examples 21, 24, and 37 at Table 7 of Watanabe et al, U.S. Pat. No. 4,214,054.

Accordingly, the need exists in the art for low cost volatile blowing agents which can be used to expand olefin polymers and yet exhibit a high degree of dimensional stability with minimal shrinkage during aging or curing of the polymer foams.

In accordance with the present invention, moldable foam beads comprising a silane-modified, crosslinked polyolefin foam are produced by Method A, which comprises the steps of:

Method A

(a) mixing a composition comprising a silane-modified polyolefin, a silanol condensation catalyst, and other desired additives in an extruder to produce a melt;

(b) injecting a blowing agent into the melt at a rate effective to produce the desired foam density in the extrudate;

(c) extruding the melt into a pressurized zone and cutting it to form crosslinkable non-foamed foamable polyolefin

beads (the term "beads" is meant to denote particles of any configuration);

(d) exposing the crosslinkable foamable polyolefin beads to moisture to produce silane crosslinking of the foamable polyolefin beads;

(e) adjusting the temperature of the crosslinked foamable polyolefin beads to a suitable and effective foaming temperature; and

(f) expelling the crosslinked foamable polyolefin beads to a zone of lower pressure that will cause them to expand and form foam beads.

In accordance with the present invention, moldable foam beads comprising a crosslinked polyolefin foam are also produced by Method B, which comprises the steps of:

Method B

(a) mixing a composition comprising a polyolefin, a chemical crosslinking agent, and other desired additives in an extruder to produce a melt;

(b) injecting a blowing agent into the melt at a rate effective to produce the desired foam density in the extrudate;

(c) extruding the melt into a pressurized zone and cutting it to form crosslinkable, non-foamed, foamable polyolefin beads;

(d) exposing the crosslinkable foamable polyolefin beads to sufficient temperatures to produce crosslinking of the foamable polyolefin beads;

(e) adjusting the temperature of the crosslinked foamable polyolefin beads to a suitable and effective foaming temperature; and

(f) expelling the crosslinked foamable polyolefin beads to a zone of lower pressure that will cause them to expand and form foam beads.

eliminates the need for a high energy radiation source for crosslinking and will give more uniform crosslinking throughout the foam in comparison to the radiation method, as radiation does not easily penetrate relatively thick (1/8" - 1/2") foam.

The beads made by this invention are non-crosslinked or crosslinked, as desired and are expanded as they leave the apparatus into a zone of lower pressure, which eliminates the need for large autoclave type reactors. The use of heat activated chemical crosslinking or silane crosslinking eliminates the need for a preprocessing crosslinking step. The beads made in this manner do not require the pre-molding pressurizing step used in the autoclave blowing agent impregnation process.

The entire system needed to make these moldable thermoplastic polymers, such as non-crosslinked and crosslinked polyolefin beads, can be installed at the molding facility and sized according to the molder's needs. Using the apparatus and method disclosed in this invention, the molder can produce the quantity of beads as needed to fill orders. Crosslinking, when required, takes place in the apparatus, and expansion occurs as the beads leave the apparatus. The storage time required, by some methods, to age the beads is eliminated or significantly less, and the space than that required for storing large volumes of expanded beads purchased from current suppliers is less. Having the bead manufacturing equipment at the molding site eliminates the high cost associated with shipping large quantities of the low bulk density beads. In addition, since the molder is producing his own beads, he has complete control over the moldable bead specifications, such as density, color, additives, crosslinked level, etc., and these can be changed relatively easily as needed.

In the production of the heat activated, chemically crosslinked polyolefin foams or silane-crosslinked polyolefin foams of the present invention where silane-modified polyolefins are used, polyolefins are selected from

homopolymers and copolymers of ethylenically-unsaturated monomers having from 2 to about 8 carbon atoms, such as ethylene, propylene, butenes, pentenes, hexenes and the like. The copolymers can include other compatible monomers, as described below. Presently, the polyethylene-type polymers are preferred, and such polymers are referred to in the disclosure and examples below, but this should be regarded as exemplary of the invention rather than limiting in any sense. Particularly preferred are the polyethylenes, including medium density polyethylene, low density polyethylene, and linear low density polyethylene. Such polyethylenes are described in the Kirk-Othmer Encyclopedia of Chemical Technology, Third Ed., Vol. 16, pages 385-420, the Modern Plastics Encyclopedia 1986-87, pages 52-63 and in the Encyclopedia of Polymer Science and Technology, Vol. 7, page 610.

The term "silane-modified polyethylene resin", as used in the present specification and the appended claims, denotes a modified polyethylene resin obtained by chemically bonding a silane compound containing at least one unsaturated group to a polyethylene-type resin in the presence of a radical generator, as disclosed, for example, in U.S. Pat. No. 4,160,072.

The term "polyethylene resin", as used in the present specification and the appended claims, is meant to include not only homopolymers of ethylene, but also ethylene copolymers composed of at least 50 mole percent, and preferably at least 70 mole percent, of an ethylene unit and a minor proportion of a monomer copolymerizable with ethylene, and blends of at least 50 percent by weight, preferably at least 60 percent by weight, of the ethylene homopolymer or copolymer with another compatible polymer.

Examples of monomers copolymerizable with ethylene and other olefins, are vinyl acetate, vinyl chloride, propylene, butene, hexene, acrylic acid and its esters, and methacrylic acid and its esters. The other polymer that can be blended with the ethylene homopolymer or copolymer may be any

polymer compatible with it. Some examples of compatible polymers include polypropylene, polybutadiene, polyisoprene, poly-chloroprene, chlorinated polyethylene, high density polyethylenes, polyvinyl chloride, a styrene/butadiene copolymer, a vinyl acetate/ethylene copolymer, an acrylonitrile/butadiene copolymer, a vinyl chloride/vinyl acetate copolymer, etc. Especially preferred species are polypropylene, polybutadiene and styrene/butadiene copolymer.

Examples of polyethylene resins that can be advantageously employed in the present invention are low-, medium-, and high-density polyethylenes, an ethylene/vinyl acetate copolymer, an ethylene/propylene copolymer, copolymers of ethylene and methyl or ethyl acrylate, a blend of polyethylene and polypropylene, a blend of polyethylene and ethylene/vinyl acetate copolymer, and a blend of polyethylene and an ethylene/propylene copolymer. Of these, a medium density polyethylene, low density polyethylene, and ethylene/propylene copolymers are especially suitable.

Preferably, the polyethylene resins have a softening point of less than 130° C. Furthermore, it is preferred that the polyethylene resin have a melt index of 0.2 to 20, preferably 0.3 to 6 decigrams per minute, and a density of 0.910 to 0.940, preferably 0.916 to 0.925 grams/cc.

In the present invention, the silane-modified polyolefin resin is prepared by chemically bonding a silane compound containing at least one unsaturated group to the polyolefin resin described above in the presence of a radical generator. The silane compounds used in this invention are organosilicon compounds containing at least one unsaturated group capable of being chemically bonded to the sites of free radicals generated in the polymer chain of the polyolefin as a result of radical reaction. Several examples of such compounds are described in U.S. Pat. No. 4,160,072, and typically include organosilane compounds of the following formula:

$$\begin{array}{ccc} & R_1 & \\ & | & \\ R_2 -- & Si & -- R_4 \\ & | & \\ & R_3 & \end{array}$$

wherein one or two, preferably only one, of R_1, R_2, R_3 and R_4 represent a hydrocarbyl or hydrocarboxyl group containing a radical-polymerizable double bond, and the rest represent organic residues capable of being split off by hydrolysis.

In the above formula, examples of the hydrocarbyl group containing a radical-polymerizable double bond are vinyl, allyl, 2-methylallyl, butenyl, cyclohexenyl, cyclopentadienyl, and octadienyl, and examples of the hyrocarboxyl group containing a radical-polymerizable double bond include allyloxy and 2-methyl allyloxy. Other examples include:

$$\begin{array}{l} \qquad\ \ CH_3 \\ \qquad\ \ \ | \\ CH_2 = C - COOCH_2CH_2CH_2- \ , \end{array}$$

$$\begin{array}{l} \qquad\ \ CH_3 \\ \qquad\ \ \ | \\ CH_2 = C - COOCH_2CH_2OCH_2CH_2CH_2- \ , \text{ and} \end{array}$$

$$\begin{array}{l} \qquad\ \ CH_3 \qquad\qquad\qquad\quad OH \\ \qquad\ \ \ | \qquad\qquad\qquad\qquad\ \ | \\ CH_2 = C - COOCH_2OCH_2CHCH_2OCH_2CH_2CH_2- \end{array}$$

Of these, vinyl is most preferred.

Examples of the organic residues capable of being split off by hydrolysis include alkoxy groups such as methoxy, ethoxy or butoxy; acyloxy groups such as formloxy, acetoxy or propionoxy; oxime groups such as: